SEPARATION AND ANALYSIS OF HYDROXYAROMATIC SPECIES IN LIQUID FUELS. I. ANALYTICAL METHODOLOGY

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INTRODUCTION

The analysis of hydroxyaromatics (ArOH) in fuels has received considerable attention for the last 20-30 years. Interest was especially high in the late 1970's and early 1980's during the "synfuels boom" because of the relatively high concentrations of ArOH in shale oils and especially coal liquids. ArOH as a class are important because they impact fuel properties such as its stability, viscosity, water miscibility and toxicity as well as its behavior in refinery processes. For example, Hara, *et al.* (1) and White *et al.* (2) found that phenolic compounds contributed to sediment formation in SRC-II coal liquid through oxidative coupling. In addition, ArOH are believed to increase viscosity by hydrogen bonding to nitrogen bases (3). Finally, ArOH and cyclic ethers are believed to control the rate of hydrodeoxygenation of coal liquids during hydrotreating processes (4).

The approach most commonly used for analysis of ArOH involves a preliminary step for their isolation from the bulk fuel matrix followed by analysis of the ArOH concentrate. Aqueous extraction and liquid chromatography are the most common methods for isolating ArOH; GC, GC/MS, MS, NMR, IR, and UV have all been used singly or in combination for analysis of the ArOH concentrate.

While any of the published methods will work on fuels rich in ArOH, unsatisfactory results are often obtained on samples such as petroleum which are low in ArOH as well as with samples with a higher average molecular weight or boiling point. For example, aqueous-alcoholic NaOH extraction yields negligible amounts of acidic material from high-boiling petroleum distillates and residues which actually contain 10-20 weight-percent acidic compounds (5). The hydrophobic nature of larger molecular weight acids prevents them from partitioning into the aqueous phase.

Liquid chromatography on alumina probably has the widest applicability for isolation of ArOH from fuels (6-11), although methods using silica as the adsorbent have also been reported (11-17). Reportedly, the silica-based methods have yielded ArOH fractions also containing nitrogen compounds (11,13, 14) but Schabron *et al.* (16) and Hurtubise *et al.* (17) reported that pretreating the silica with HCl eliminates this problem by forming HCl-salts of nitrogen bases on the column, thereby preventing their coelution with ArOH. Coelution of nitrogen compounds with ArOH has also been reported to be a problem with alumina-based separations (10,15). On the other hand, nonaqueous ion exchange chromatography has been used to obtain ArOH concentrates, either

by sequential elution of the ion exchange resin (3,18,19) or by subfractionation of the total acid concentrate on alumina (20,21). Since nitrogen bases are trapped by a cation resin and ArOH by an anion resin in that procedure, overlap of those classes is minimal. Finally, size exclusion chromatography with THF eluent separates ArOH as a class from coal liquids (22,23). Reportedly, phenols hydrogen bond to THF, thereby effectively increasing their molecular size and decreasing their elution volume from the size exclusion column.

Chemical derivatization of ArOH often facilitates subsequent chromatographic and/or spectroscopic analysis. Acylation with fluorinated acid anhydrides or acid chlorides has been used in conjunction with GC (24) and especially NMR methods (25-29). This reaction has also been used extensively to determine primary aromatic amines in coal liquids. Similarly, silylation with a variety of reagents enables specific ArOH analysis by NMR (13,30) and GC/MS (31,32). Chemical derivatization is useful from both qualitative and quantitative standpoints because 1) it eliminates many potential O-containing interfering compound classes which will not react (*e.g.*, ketones, ethers), 2) it adds a chemical moiety containing elements not commonly in fuels (*e.g.* F,Si) allowing for specific detection of ArOH, 3) it significantly adds to the molecular weight of the ArOH which facilitates mass spectral analysis because the derivatized ArOH molecular ions are at significantly higher mass than interfering compounds, 4) it improves gas chromatographic resolution of ArOH, and 5) it alters the polarity of ArOH which can enable their further separation from interfering compound classes.

The ArOH analysis method described here is based on 1) initial isolation of a total acid concentrate by nonaqueous ion exchange chromatography, 2) subfractionation of the acids into compound class fractions by HPLC, 3) chemical derivatization via acylation or silylation, and 4) GC/MS analysis of the derivatized ArOH concentrate. The objective of the scheme is to provide detailed analysis of ArOH species regardless of fuel type and overall concentration of ArOH present. Because the ultimate analysis is by GC/MS, the method is limited to distillates boiling below approximately 500° C (932° F).

Nonaqueous ion exchange chromatography was chosen for the first step because it separates acidic types from the bulk hydrocarbon matrix as well as from basic nitrogen compounds. As discussed previously, many of the published schemes based on silica or alumina overlap some nitrogen compound types into the ArOH fraction. This presents a serious interference for GC/MS analysis because nitrogen compounds yield even-numbered fragments which can partially or completely obscure parent ArOH ions. Chemical derivatization alone frequently cannot compensate for this interference because many N-compounds also derivatize. HPLC was chosen over the previously cited open-column separation methods for subfractionating acids because of its higher chromatographic resolution, use of automated instrumentation, use of detectors which continuously monitor the separation, and microprocessor-controlled solvent gradient and pump. The above factors coupled with the fact that a single column may be used for numerous samples result in much higher quality, more reproducible ArOH concentrates. This dual-liquid chromatographic approach has the following inherent advantages: 1) acidic compounds are concentrated in the first step from bulk fuel components and then subfractionated in a second step -- this approach is especially suited to fuels which contain low amounts of ArOH, 2) extremely hydrophobic or hydrophilic ArOH which are incompletely recovered

in aqueous extraction procedures pose no special problems for this procedure, 3) the complementary selectivities of the ion exchange and HPLC separations yield ArOH concentrates relatively free of other compound classes, 4) it has been evaluated using numerous pure compounds as well as a wide variety of fuels, and 5) it yields concentrates of other major acidic compound classes suitable for detailed analysis.

EXPERIMENTAL

Preliminary Fractionation of Fuels

Details of distillation (4,33) and nonaqueous ion exchange isolation of acid concentrates (5) appear elsewhere. Distillation was not absolutely necessary for analysis of ArOH, but the level of information obtained on higher boiling ArOH was enhanced if the bulk of the phenols and indanols/tetralinols were distilled into a light (*ca.* 200-325° C) boiling fraction.

Preparative HPLC Subfractionation of Acid Concentrates

A preliminary evaluation of HPLC methods for acid subfractionation (34) and a study of the liquid chromatographic behavior of acidic compounds on silica using mobile phases spiked with tetraalkylammonium hydroxides (35) give background information on the HPLC method used here. Table 1 shows details of the equipment and conditions for the acid subfractionation.

TABLE 1. Conditions for HPLC Subfractionation of Acid Concentrates

Column - 30 cm X 2.5 cm (I.D.) 316 ss
Packing-Adsorbosil-LC (Alltech Assoc. ~10μ prep grade silica)
N (average plates/m) - 15,000-20,000
Flow rate - 28 mL/min
Chart speed - 0.5 cm/min
Temperature - 35.0° C
Detector (uv) - ISCO UA-5, 1 mm path cell, 280 nm, 0-2 AUFS
Apparatus - Spectra Physics M8000 HPLC
Injection vol (mL) - 1.8
Injection amount (mg) - 300
Gradient - (linear)

	Volume Percent		
Time (min)	A	B	C
0	88	12	0
2	88	12	0
17	78	22	0
30	20	80	0
38	20	80	0
50	0	30	70
51	0	30	70
53	88	12	0

A: Methyl t-butyl ether (MTBE)
B: 70 percent ($^{V}/_{V}$) MTBE, 30 percent ($^{V}/_{V}$) methanol, 0.03 percent tetramethylammonium hydroxide
C: Methanol with 0.03 percent tetramethylammonium hydroxide.

Chemical Derivatization of ArOH

Acylations were done at room temperature by bubbling trifluoroacetyl chloride (TFACl) (SCM Speciality Chemicals, Gainsville, FL) into 0.5 mL of benzene containing 0.05 M triethylamine catalyst and 1-2 mg ArOH for 30 minutes. Nitrogen gas was passed through the reacted ArOH for 10 minutes to remove residual TFACl, and the reaction mix was transferred to a 1-mL propylsulfonic acid-bonded silica cartridge (PRS Bond Elute, Analytichem International, Harbor City, CA) and eluted with 10 mL dichloromethane. The bonded silica cartridge removed triethylamine catalyst and trifluoroacetic acid produced as a by-product from reaction of TFACl and water. Either of the above contaminants gave rise to a large, poorly eluting GC peak which interfered with analysis of C_0-C_3 phenols.

Silylation was accomplished by heating a mixture of 0.5 mL BSTFA containing 10 percent TMCS catalyst (N,O-bis(trimethylsilyl)-trifluoroacetamide, 10 percent trimethylchlorosilane; Regis Chemical, Morton Grove, IL) and 4 mg ArOH dissolved in 1.0 mL benzene at 60° C for one hour.

The silylated and acetylated ArOH were concentrated to 0.1-0.2 mL under nitrogen prior to injection into the GC.

GC/MS

A Kratos (Ramsey, NJ) MS-80 GC/MS system comprised of a Carlo Erba model 4662 temperature programmed GC, Scientific Glass Engineering (Austin, TX) open-split interface, EI source, MS-80 magnetic-scan mass spectrometer and Data General Nova 4-based DS-55 data system was used for all analyses. A 0.25 mm X 30 m, 0.25 μm film thickness J and W (Rancho Cordova, CA) DB-5 column was programmed from 50° C (initial time one minute) at a 5° C/min to 350° C (hold 20 minutes) for a typical ArOH concentrate. Other instrumental conditions were: injector - 300° C, 100:1 split; GC/MS interface - 300° C, He make up 1 mL/min (50 mL/min for solvent peak purge); column head pressure 1.25 Kg/cm^2 (1 mL/min He); mass spectral conditions - 70 eV ionizing voltage, 1,000 dynamic resolution, 0.5 sec/decade scan rate, source pressure 5 X 10^{-6} torr, and source temperature 300° C.

RESULTS AND DISCUSSION

HPLC Acid Subfractionation

Figure 1 shows UV detector traces from HPLC separation of typical acid concentrates obtained by nonaqueous ion exchange as well as a chromatogram of a synthetic blend (STD) of acidic compounds typical of those in fuels. Strong and weak acid concentrates are obtained from ion exchange separation of distillation residues (5); thus, Figure 1 shows traces from subfractionation of strong and weak acids from SRC-II >325° C and OSCR shale oil >200° C residues whereas total acids were separated from the Wilmington, CA, 370-535° C petroleum distillate.

As indicated in the figure, five or six subfractions are typically obtained from this separation. Fraction 1 contains very weak acids as well as any neutral compounds present as contaminants from the ion exchange procedure.

Fraction 2 is largely made up of pyrrolic benzologs. For example, GC/MS analysis of fraction 2 from the SRC-II >325° C weak acid concentrate showed it to contain largely C_0-C_4 carbazoles.

Originally, fraction 3 was isolated because it was uncertain whether this retention region would contain hindered phenols, strongly retained pyrrolic benzologs, or possibly amides (see corresponding compounds eluting in STD in Figure 1). Subsequent analysis of this fraction revealed it to usually contain hindered phenols; hence in much of the authors' current work, fraction 3 is combined with fraction 4 -- the main ArOH subfraction. Cut points for fraction 4 are usually defined by retention of 2,4,5-trimethylphenol and 2-naphthol (see STD, Figure 1). However, as indicated in the figure, sometimes the final cut point is extended beyond this range during separation of synthetic fuels or other fuels not likely to contain carboxylic acids. Subsequent work (35) with a chloroform-based mobile phase has indicated that much of the retention of polycyclic ArOH beyond that of 2-naphthol is due to their poor solubility in methyl t-butyl ether (MTBE). Hence, conditions specified in Table 1 are no longer used for subfractionation of nondistillable acids. Instead, an analogous mobile phase system is used where chloroform is substituted for MTBE as the bulk solvent. Details of this separation are available (36).

In separations of petroleum acid concentrates (Figure 1, Wilmington 370-535° C), fraction 5 cut points are set such that it will contain the bulk of the carboxylic acids present. A later eluting fraction 6 is then obtained which contains either very acidic (*i.e.*, condensed aromatic) carboxylic acids, dicarboxylic acids, and/or polyfunctional compounds. With synfuels, all compounds more retained than ArOH are usually lumped into the fifth subfraction. This subfraction probably contains dihydroxyaromatics as well as hydroxylated nitrogen heterocycles (35), such as those recently identified in a SRC-II coal liquid (37). As expected, weak acid concentrates show very little material eluting in fractions 4-6.

As stated previously, one of the objectives of the liquid chromatographic separations was to obtain ArOH fractions relatively free of nitrogen compounds. Figure 2 shows that this objective was largely met as evidenced by the dual FID/NPD GC chromatograms of representative ArOH subfractions. The sensitivity ratio of the FID/NPD detectors was adjusted such that carbazole gave an FID/NPD response ratio of two. The largest concentration of nitrogen compounds observed was in the fraction from OSCR shale oil. This observation is consistent with relatively high concentrations of amides such as 2-hydroxy pyridines in shale oil (21,38). Amides with two free hydrogens (*e.g.* benzamide) and amides analogous to 2-hydroxypyridine are known to elute into the ArOH subfraction in this HPLC system (35).

Chemical Derivatization

Tables 2 and 3 show yields of silylated and acylated hydroxy compounds, respectively. The highly hindered 2,4,6-tri-t-butylphenol did not react in either system, but most other ArOH reacted in good yield in both systems. As shown by Table 3, use of 6:1 molar ratio of catalyst to ArOH gave improved yields over those obtained using a 0.6:1 ratio. Triethylamine serves a dual role as catalyst and HCl scavenger (25,26); thus, an excess is necessary for quantitative yields.

TABLE 2. - Results of BSTFA silylation of pure alcohols and hydroxyaromatics[1]

Compound	Percent Reacted
Alcohols	
1-Dodecanol	99.9
9-Hydroxyfluorene	99.7
1-Acenaphthenol	100.0
Hydroxyaromatics	
o-Cresol	98.3
2,6-Dimethylphenol	99.9
2,4,6-Tri-t-butylphenol	0
2-Naphthol	99.8
Dihydroxyaromatics	
Resorcinol	0,100[2]

[1] 10 Percent trichlorosilane catalyst.

[2] The first number indicates percentage reacted at one OH, the second number indicates the percentage reacted at both OH-sites.

GC/MS

Figures 3 and 4 show total ion current GC/MS profiles of ArOH, acylated ArOH, and silylated ArOH in SRC-II 200-325° C distillate and >325° C residue, respectively. Inspection of the figures and analysis of the resulting data lead to the following conclusions. 1) Acylated ArOH are more volatile than their underivatized counterparts while silylated ArOH are less volatile than plain ArOH. 2) Chemical derivatization greatly improves gas chromatographic resolution of ArOH on nonpolar columns. This feature is especially obvious in Figure 4, where the resulting mass spectra from the underivatized ArOH run were so complex they were essentially unanalyzable. Even in the case of the low boiling SRC-II ArOH (Figure 3), many more isomers of a given ArOH homolog were observed in GC/MS runs of derivatized ArOH. For example, only two C_2-phenols were resolved in GC/MS of underivatized ArOH (Figure 3A), whereas six were detected during analysis of both the acylated (Figure 3B) and silylated ArOH (Figure 3C). In the case of C_3-phenols, the number of isomers resolved in Figures 3(A-C) were 4, 9, and 5, respectively. 3) Mass spectra from acylated ArOH are much more characteristic and therefore more useful for qualitative identification of ArOH than either silylated or underivatized ArOH. However, silylated ArOH give stronger parent (M+) and M-15 ions which enables more sensitive detection of minor components in ArOH subfractions. These points are discussed in detail below.

TABLE 3. - Results of TFACl acylation of pure alcohols and hydroxyaromatics

Compound	Catalyst ratio [1] 0	0.6	6
	Percent Reacted		
Alcohols			
1-Dodecanol	100	100	100
9-Hydroxyfluorene	77	100	--
1-Acenaphthenol	10	100	--
Hydroxyaromatics			
o-Cresol	<1	43	100
2,4-Dimethylphenol	<1	80	100
2,6-Dimethylphenol	<1	8	100
2,4-Dimethyl-6-t-butylphenol	0	0	48
2,4,6-Tri-t-butylphenol	--	0	0
2-Hydroxybiphenyl	0	40	100
2-Naphthol	<1	89	98
9-Phenanthrol	<1	100	--
Dihydroxyaromatics			
Catechol	2,0[2]	15,79[2]	--
Resorcinol	0	12,88[2]	0,100

[1] Molar ratio of triethylamine catalyst to reactant.
[2] The first number indicates percentage reacted at one OH; the second number number indicates the percentage reacted at both OH-sites.

Figures 5 and 6 show mass spectra of individual peaks from GC/MS of ArOH fractions from fuels. Figures 5 (A-C) show representative spectra of phenol, a cresol and a C_2-phenol from silylated ArOH isolated from Wilmington <370° C distillate. Obviously, the dominant ions in the spectra are the parent ions (M+), M-15 ions produced from loss of a methyl group from the trimethylsilyl ether moiety, and m/e 73 ions from $(CH_3)_3Si+$. Spectra in Figures 5 (D-F) are all C_2-phenols obtained from GC/MS of acylated ArOH from the same Wilmington distillate. Parent ions (m/e 218) are certainly intense in the acylated C_2-phenols, but they do not overshadow the fragment ions to the extent observed in spectra of silylated ArOH. Also, M-97 ions (m/e 121) representing loss of the $CF_3C(O)O+$ functionality are apparent as well as m/e 69 ions from CF_3+. More importantly, loss of CH_3 in the ethylphenol (Figure 5F) can be used to distinguish it from dimethylphenols (Figures 5D and 5E) in the acylated fraction, whereas all silylated C_2-phenols show M-15 ions. Furthermore, spectra of the two acylated dimethylphenols are easily distinguished by the presence of the m/e 175 ion in only one as well as the large difference in intensity of the m/e 121 ion. Thus, Figure 5 demonstrates the greatly enhanced utility of acylation over silylation for identification of specific ArOH isomers. On the other hand, GC/MS of underivatized Wilmington <370° C

ArOH resolved only one cresol and only one C_2-phenol; thus, no isomeric information was obtained whatsoever from that analysis. All three cresols and up to six C_2-phenols have been observed from GC/MS of derivatized ArOH.

Figure 6 further illustrates points made by Figure 5; also, it shows the need for standard spectra of acylated ArOH to aid in identification of ArOH in fuels. Figures 6A and 6B show spectra of two C_2-indanols and Figure 6C shows a C_1-tetralinol from analysis of acylated SRC-II 200-325° C ArOH. Figure 6C can be identified as a 2- or 3-methyltetralinol by the fragment ion at m/e 216 produced from retro-Diels-Alder loss of propylene from the methyl-substituted six-membered saturated ring (39). Indanols do not show this type of fragmentation, but do readily lose any alkyl groups substituted onto the cyclopentyl ring. Thus, Figure 6A shows a C_2-indanol with one methyl group on the saturated ring (M-15 = 243) and Figure 6B shows what is probably an indanol with an ethyl group substituted on the cyclopentyl ring (m-29 = 229). With a sufficient library of standard acylated ArOH spectra, identification of a large number of phenol and indanol/tetralinol isomers would be possible.

Figures 6 (D-F) further emphasize the need for standard spectra. These spectra show mass 280 (184 underivatized) members of the $C_nH_{2n-14}O$ series from OSCR >200° C shale oil (6D), SRC-II 200-325° C (6E) and SRC-II >325° C (6F) acylated ArOH fractions. Possible structures for this series include: hydroxybiphenyls, hydroxyacenaphthalenes, benzindanols and benztetralinols. Although the spectra in Figures 6 (D-F) are distinctively different, it is quite difficult to definitively assign a structure to each because of the lack of reference spectra. Usually, this series is referred to as hydroxybiphenyls in the literature; but, considering the differences in these and many other spectra not shown it appears very doubtful that all members of this series are hydroxybiphenyls. After phenols and indanols/tetralinols, this series is the most abundant in most ArOH concentrates. Current best guesses at assignment of Figures 6(D-E) are: (6D) C_1-hydroxybiphenyl, (6E) C_1-2-hydroxybiphenyl, and (6F) C_1-hydroxyacenaphthalene.

CONCLUSIONS

The combined liquid chromatographic-chemical derivatization-GC/MS approach can provide a detailed analysis of ArOH in fuels boiling below 500° C. Acylation is usually the preferred derivatization method because it enhances the volatility of ArOH and provides the most useful mass spectra for compound identification. Currently, the greatest limitation on the method is the unavailability of standard spectra for acylated ArOH. Part 2 of this series presents results from detailed analysis of ArOH from SRC-II coal liquid, OSCR shale oil and Wilmington, CA, petroleum (40).

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REFERENCES

1. Hara, T., L. Jones, N. C. Li and K. C. Tewari, Fuel, 60 (1981) 1143.
2. White, C. M., L. Jones and N. C. Li, Fuel, 62, (1983) 1397.
3. Young, L-J. S., T. Hara and N.C. Li, Fuel, 63, (1984) 816.
4. Green, J. B., P. L. Grizzle, J. S. Thomson, R. J. Hoff and J. A. Green, Fuel, in press.
5. Green, J. B., R. J. Hoff, P. W. Woodward and L. L. Stevens, Fuel, 63, (1984) 1290.
6. Later, D. W., M. L. Lee, K. D. Bartle, R. C. Kong, and D. L. Vassellaros, Anal. Chem., 53, (1981) 1612.
7. Schiller, J. E., and D. R. Mathiason, Anal. Chem., 49, (1977) 1225.
8. Snyder, L. R., B. E. Buell and H. E. Howard, Anal. Chem., 40, (1968) 1303.
9. Boduszynski, M. M., R. J. Hurtubise and H. F. Silver., Anal. Chem., 54 (1982) 372 and 375.
10. Oderfer, G. A., L. R. Rudnick and D. D. Whitehurst, Amer. Chem.Soc., Div. Fuel Chem. Prepr., 22(2) (1981) 89.
11. Whitehurst, D. D., S. E. Butrill, F. J. Derbyshire, M. Farcasiu, G. A. Oderfer and L. R. Rudnick, Fuel, 61 (1982) 994.
12. Farcasiu, M., Fuel, 56 (1977) 9.
13. Seshadri, K. S., D. C. Young and D. C. Cronauer, Fuel, 64 (1985) 22.
14. Seshadri, K. S., and D. C. Cronauer, Fuel, 62 (1983) 1436.
15. McClennen, W. H., H. L. C. Meuelaar, G. S. Metcalf and G. R. Hill, Fuel, 62 (1983) 1422.
16. Schabron, J. F., R. J. Hurtubise and H. F. Silver, Anal. Chem., 51, (1979) 1426.
17. Hurtubise, R. J., T. W. Allen, J. F. Schabron and H. F. Silver, Fuel, 60 (1981) 385.
18. Jewell, D. M., J. H. Weber, J. W. Bunger, H. Plancher and D. R. Latham, Anal. Chem., 44, (1972) 1391.
19. White, C. M., and N. C. Li, Anal. Chem., 54 (1982) 1570.
20. McKay, J. F., T. E. Cogswell, J.H. Weber, and D. R. Latham, Fuel, 54 (1975) 51.
21. McKay, J. F., M. M. Boduszynski and D. R. Latham, Liquid Fuels Technol., 1 (1983) 35.
22. Philip, C. V., and R. G. Anthony, Amer. Chem. Soc., Div. Fuel Chem. Prepr., 24(3) (1979) 204.
23. Philip, C. V., and R. G. Anthony, Fuel, 61 (1982) 357.
24. Shulgin, A. T., Anal. Chem., 36 (1964) 920.
25. Sleevi, P., T. E. Glass and H. C. Dorn, Anal. Chem., 51 (1979) 1931.
26. Dorn, H. C., P. S. Sleevi, K. Koller and T. Glass, Amer. Chem. Soc., Div. Fuel Chem. Prepr., 24(2) (1979) 301.
27. Baltisberger, R. J., K. M. Patel, V. I. Stenberg and N. F. Woolsey, Amer. Chem. Soc., Div. Fuel Chem. Prepr., 24(2) (1979) 310.
28. Burke, F. P., R. A. Winschel and G. A. Robbins, "Recycle Slurry Oil Characterization," Final Rept. on U.S. Dept. Energy Contract No. DE-AC22-80PC30027, NTIS, 1985, p. 50.
29. Spratt, M. P. and H. C. Dorn, Anal. Chem., 56, (1984) 2038.
30. Schweighardt, F. K., C. M. White, S. Friedman and J. L. Shultz, in "Organic Chemistry of Coal," J. W. Larsen (ed.), American Chemical Society, Washington, DC, 1978, pp. 240-257.
31. Novotny, M., J. W. Strand, S. L. Smith, D. Wiesler and F. J. Schwende, Fuel, 60 (1981) 213.

32. Nishioka, M., M. L. Lee, H. Kudo, D. R. Muchiri, L.J. Baldwin, S. Pakray, J. G. Stuart, and R. N. Castle, Anal. Chem., 57 (1985) 1327.
33. Hirsch, D. E., J. E. Dooley, H. J. Coleman and C. J. Thompson, "Compound-Type Separation and Characterization Studies for a 370-535° C Distillate of Wilmington, Calif., Crude Oil," U.S. BuMines Rept. of Investigation, RI 7893, 1974.
34. Green, J. B. and P. L. Grizzle, in "Trace Analysis," J. F. Lawrence (ed.), v. 2, Academic Press, New York, 1982, pp. 223-265.
35. Green, J. B., J. Chromatogr., in press.
36. Green, J. B., C. A. Treese and S. K-T Yu, "Chemical/Physical Separations of Alternate Petroleum Distillates III. HPLC Subfractionation of Acid Distillates," NIPER Topical Report No. 42, 1985.
37. Nishioka, M., R. M. Campbell, M. L. Lee, D. R. Muchiri, J. G. Stuart and R. N. Castle, Anal. Chem., 57 (1985) 2211.
38. Holmes, S. A., and L. F. Thompson, Fuel, 62 (1983) 709.
39. Wozniak, T. J., and R. A. Hites, Anal. Chem., 57 (1985) 1314.
40. Green, J. B., C. A. Treese, S. K-T Yu, J. S. Thomson, C. P. Renaudo, and B. K. Stierwalt, Amer. Chem. Soc., Div. Fuel Chem. Prepr., 31, spring 1986.

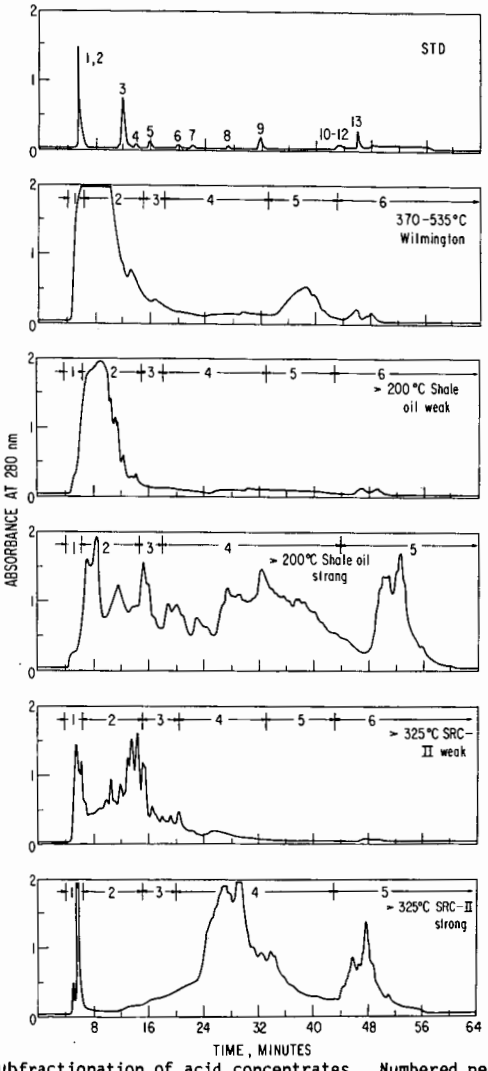

Figure 1. HPLC subfractionation of acid concentrates. Numbered peaks in STD are: 1)dibenzofuran, 2) benzophenone, 3) 13H-dibenzo[a,i]carbazole, 4) oxindole, 5) 2,4,5-trimethylphenol, 6) o-cresol, 7) 3,4- dimethylphenol, 8) phenol, 9) 2-naphthol, 10) 2,2-diphenylpropanoic acid, 11) p-toluic acid, 12) 1-fluorenecarboxylic acid, 13) 1-naphthoic acid. See text for explanation of retention regions 1-6 shown above chromatograms.

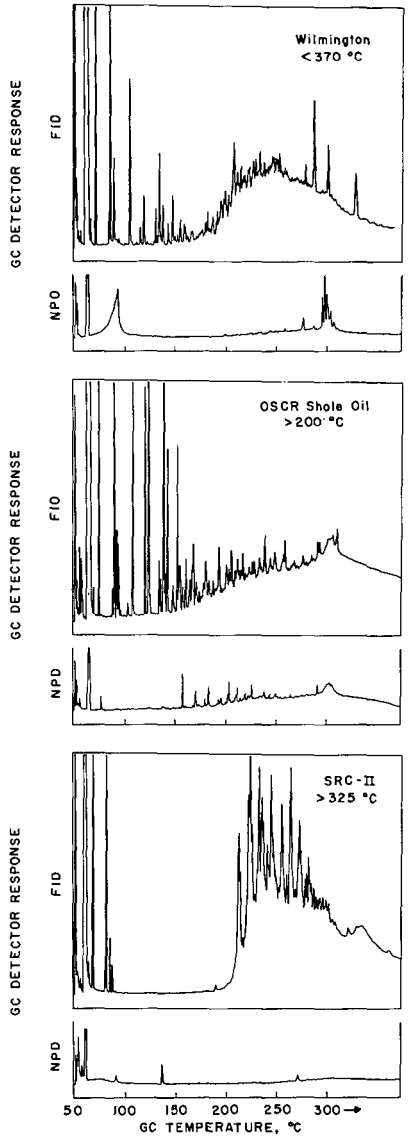

Figure 2. Gas chromatograms of selected underivatized ArOH fractions using dual FID/NPD (thermionic) detection. GC conditions were similar to those specified for GC/MS. Note the overall low levels of N-containing compounds in ArOH fractions.

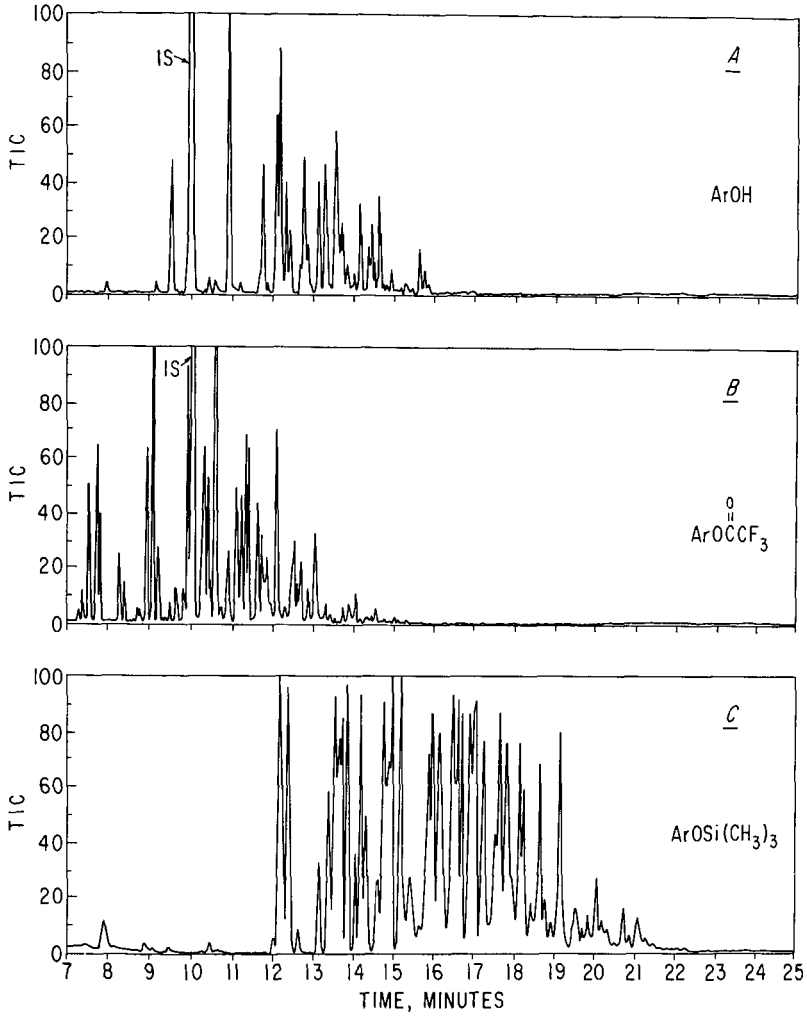

Figure 3. Total ion GC/MS traces of plain and derivatized SRC-II 200-325° C ArOH concentrate. Note the relative volatilities of acylated and silylated ArOH vs underivatized ArOH, as well as the enhanced GC resolution resulting from chemical derivatization.

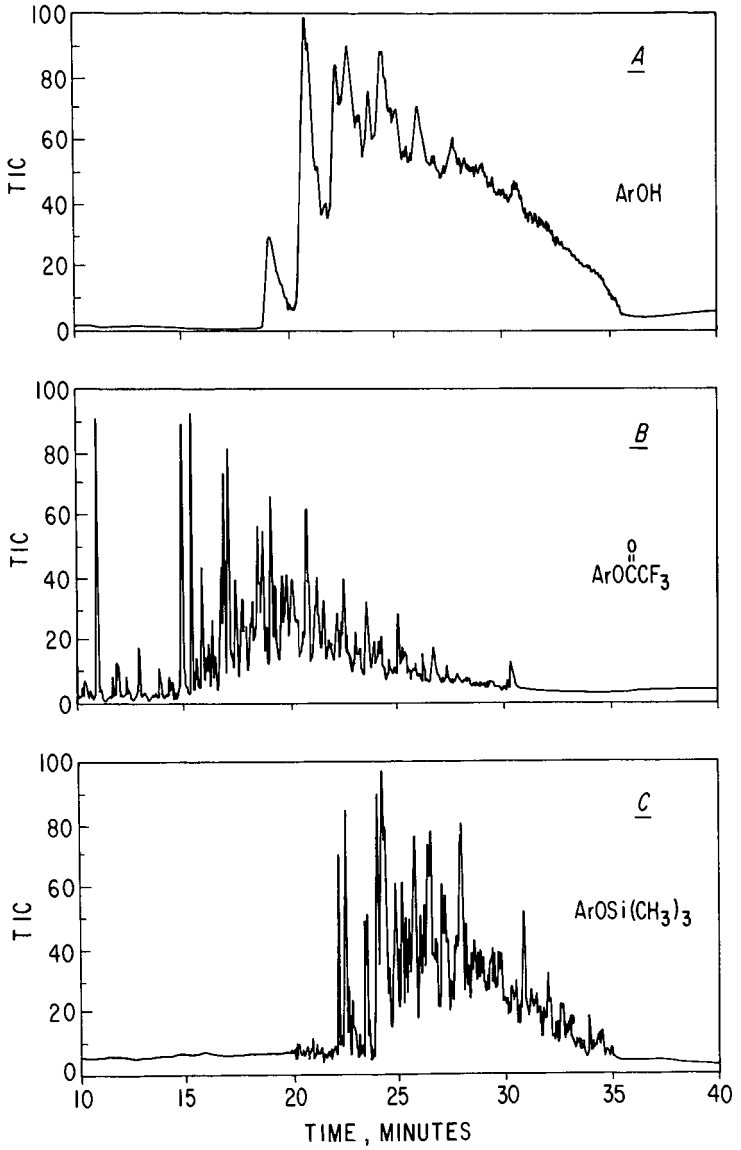

Figure 4. Total ion GC/MS traces of plain and derivatized SRC-II >325° C ArOH. The benefits of chemical derivatization are especially evident from analysis of higher boiling ArOH fractions. Higher molecular weight silylated ArOH (*e.g.* pyrenols) were not eluted from the GC column.

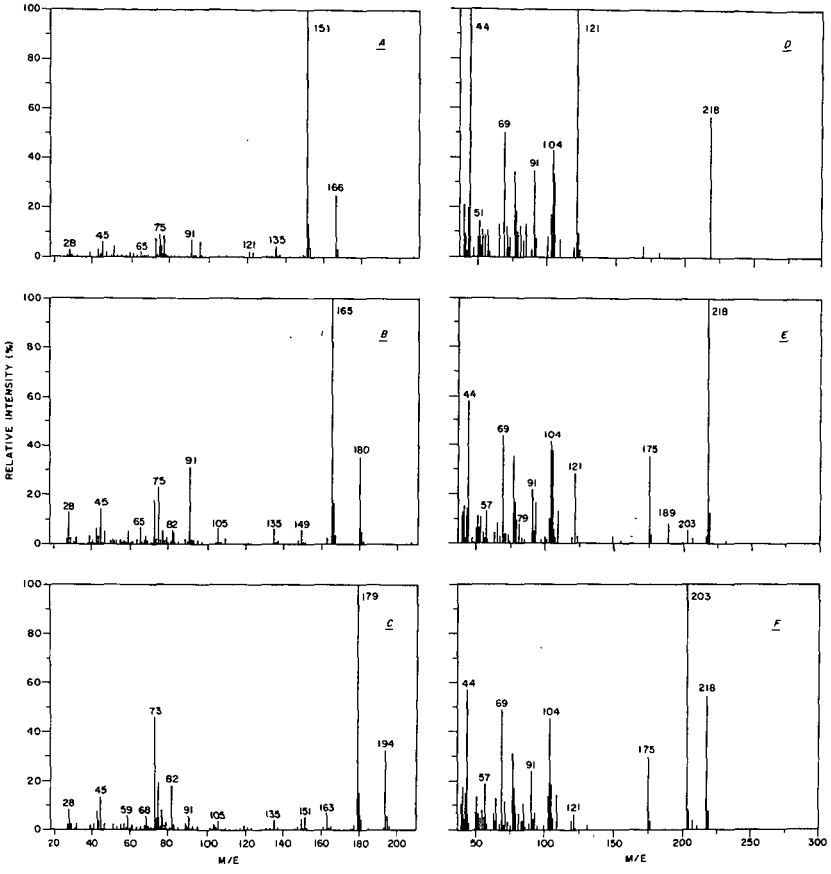

Figure 5. Mass spectra of silylated C_0-C_2 phenols (A-C) and acylated C_2-phenols (D-F) from analysis of Wilmington <370° C ArOH. Note the large M-15 fragment in A-C and see text for explanation of D-F.

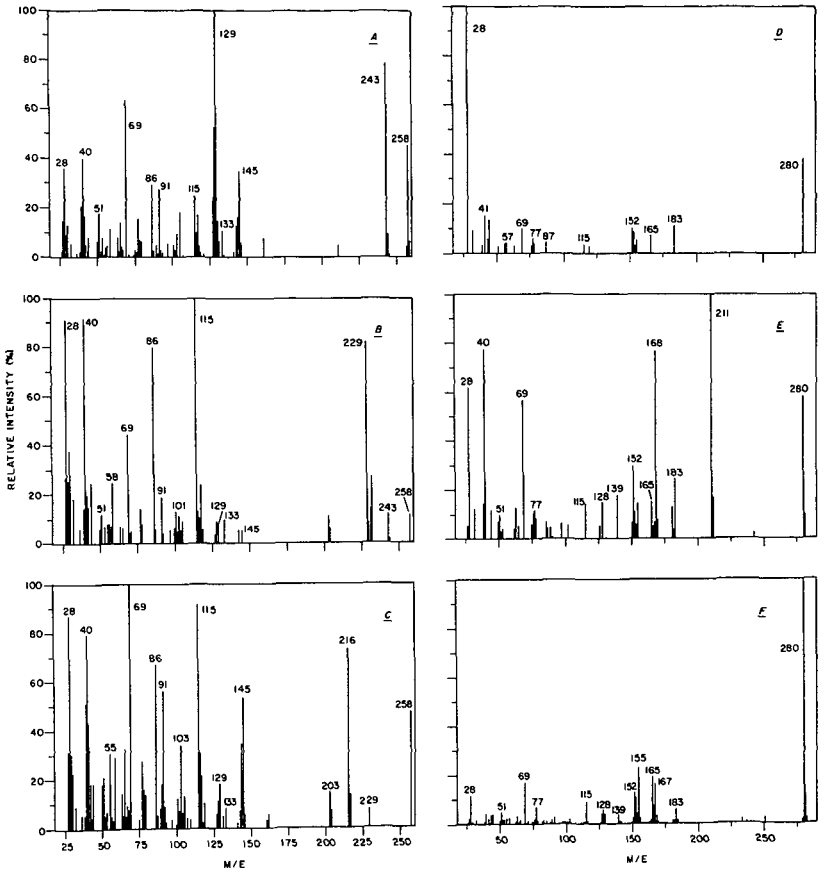

Figure 6. Mass spectra of acylated C_2-indanols (A,B) and a C_1-tetralinol (C) from SRC-II 200-325° C ArOH, and representative spectra from acylated members of the $C_nH_{2n-14}O$ series from <200° C shale oil (D), SRC-II 200-325° C (E) and SRC-II >325° C (F) ArOH fractions. See text.